Temperature dependent EXAFS analysis of structural disorder in the $Co_3O_2BO_3$ ludwigite using Monte Carlo methods and evolutionary algorithm

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Homometallic ludwigites with chemical formula $(M^{2+})(M^{3+})O_2BO_3$ are mixed-valent complex oxides with potentially interesting physical phenomena. It was recently shown that a hybrid of reduced-multiwalled carbon nanotubes and $Co_3O_2BO_3$ have outstanding performance as an oxygen evolution reaction (OER) electrocatalyst, where the slow OER kinetics presents the main bottleneck regarding the storage of renewable energy and clean energy generation [1]. The novel catalyst containing $Co_3O_2BO_3$ have an overpontential lower than that for the state-of-the-art RuO_2 catalyst [2]. The remarkable OER electrocatalyst performance of the ludwigite was mainly attributed to its local distorted octahedral environment, which increases the unit cell volume and enhances its catalytic active surface area. In addition to that, atomic positional disorder may play a significant role in the Co ludwigite unit cells volume size. However, the possibility of structural disorder in $Co_3O_2BO_3$ lacks a dedicated study in contrast to other heterometallic ludwigites, which are known to present disordered structures [3]. Finally, understanding the role of structural disorder in these materials may help the synthesis of robuster and more efficient OER electrocatalyst for green energy production.

This work investigates structural disorder in $Co_3O_2BO_3$ as a function of temperature by applying reverse Monte Carlo (RMC) methods in EXAFS (extended x-ray absorption fine structure) data analysis. The EXAFS spectra were extracted using traditional methods [4] from Co K edge X-ray absorption spectroscopy experiments performed at the XAFS2 beamline of LNLS. Then, RMC methods were applied to refine the Co ludwigite atomic position by introducing random small amounts of disorder in the system until the refined crystal structure EXAFS spectrum reproduces experimental data. In addition to that, the convergence in reasonable time of simulated results depends upon the use of an evolutionary algorithm (EA), which allows us to cover a much bigger area of the configurational space much faster than regular methods. The EXAFS-RMC/EA analysis was performed using EvAX (Evolutionary Algorithms for XAS analysis) [5].

In this work we will show experimental and simulated EXAFS for $Co_3O_2BO_3$ for various temperatures from 6 to 900 K. Simulated spectra resemble remarkably well experimental data and we discuss the influence of structural disorder on physical phenomena. We conclude that local disorder regarding Co octahedral environment is very rigid and does not change significantly up to 400 K. Above this temperature, changes in the local octahedral environment are possibly connected to two charge ordering transitions at 480 K and 500 K. Finally, x-ray powder diffraction results are discussed in the light of EXAFS data.

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